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Hydrophobic Modification of Bi₂O₃-Doped Si-Ti Composite Film on a Wood Surface

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Abstract: In order to improve the hydrophobicity of the composite film on the wood surface, the wettability of the wood surface and its morphology, chemical structure, roughness and free energy changes were investigated in this paper after modification treatments with different volume fractions of octadecyltrichlorosilane (OTS) and polydimethylsiloxane (PDMS). It can be found that the water contact angle and surface roughness of the hydrophobically modified wood increased with the increase in volume fraction, but the overall effect of OTS hydrophobic modification was better than that of PDMS, and a maximum water contact angle of up to 140.8° could be obtained at a volume fraction of 2% of OTS. In addition, the intensity of the stretching vibration peak of -OH was weakened after the modification, while the intensity of the stretching vibration peak of -CH₂- was enhanced, resulting in an increase in hydrophobicity. At the same time, it can be found that the surface free energy of the modified wood specimens was reduced, which shows that OTS and PDMS improve the surface hydrophobicity of the wood by increasing the surface roughness and decreasing the surface free energy together. Finally, the hydrophobically modified Bi₂O₃-doped silica-titanium composite film still possessed high photocatalytic degradation activity for rhodamine B and gas formaldehyde, and the degradation rate could reach more than 90%.

Keywords: Bi₂O₃; hydrophobic modification; Si-Ti composite film; wood surface



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1. Introduction

The wettability of the wood surface is one of the most important characteristics affecting the surface properties of wood and is related to the interaction between the wood surface and the liquid surface. Hydrophobicity is normally required on wood surfaces due to the numerous hydrophilic polar groups such as hydroxyl and carboxyl groups in the chemical structure of wood. On the one hand, this reduces the hygroscopicity of the wood and prevents mould and rot under humid external conditions, and on the other hand, it reduces the chances of the wood surface being contaminated by liquids, thus increasing its serviceability. Fluorinated SiO₂ coatings prepared on the surface of wood by Chien-Te Hsieh [1] et al. strongly inhibited moisture adsorption and vapour diffusion into the interior of wood with a porous structure. While moisture absorption and dimensional deformation are the main drawbacks of wood as a building material, the TiO₂ coating loaded on the wood surface by Wang et al. [2] simply processed the wood with sandpaper to create an appropriate micro- and nanocomposite structure, then coated it with a fluoroalkylsilane/silica composite suspension and dried it to form a self-healing superhydrophobic surface, which greatly improved the hydrophobic and anticorrosive properties of the wood surface.

The surface wettability of wood is influenced by the free energy of the wood surface and the surface roughness and microstructure of the surface. Methods for building superhydrophobic surface roughness of wood generally include coating, wet chemical, hydrothermal, layer-by-layer self-assembly and sol-gel methods. Yi Tan et al. [3] used hydrothermal and vacuum impregnation methods to form microstructures of ZnO rods on wood surfaces and obtained excellent wear resistance with contact angles up to 155° . Among the various methods, the sol-gel method is the most commonly used one. Wang [4] used the classical sol-gel method to synthesise SiO_2 nanoparticles to assist in the construction of surface wienner structures, which can make the wood triple-cut with superhydrophobic properties. The wood was then treated to improve its mechanical strength and hydrophobicity. Tao Yang et al. [5] used PDAD-MAC electrostatic attraction and layer-by-layer self-assembly and sol-gel binding to precipitate negatively charged silica sol into the cell walls and cavities of wood, which improved the mechanical strength and hydrophobicity of the treated wood.

However, the use of nanoparticles alone to improve the hydrophobicity of wood surfaces is limited by the presence of -OH on the surface of the particles, so researchers have introduced low surface free energy substances to further improve hydrophobicity. Liu M [6] et al. constructed a micro-nanostructure similar to the surface of a lotus leaf using a one-step hydrothermal method on the surface of the wood and grafted $-\text{CH}_2=\text{CH}_2$ to obtain a superhydrophobic surface with a high water contact angle of 153° and a very low rolling angle. In addition, the combination of polymers and inorganic particles can also build multifunctional superhydrophobic wood surfaces. Rui Yang et al. [7] used orthosilicates and polystyrene to prepare hollow-shaped microsphere structured particles; they then coated the wood surface with a polydimethylsiloxane (PDMS) resin layer to improve its surface coarse superlattice and obtained water contact angles up to 150° . Wang C [8] et al. prepared modified SiO_2 compounded with polystyrene and drop-coated it onto the wood surface to construct superhydrophobic films with a contact angle of 153° . To improve the weathering resistance of hydrophobic surfaces, Wang X [9] et al. constructed TiO_2 nanocoatings on wood surfaces using the sol-gel method and then modified them with cetyltrimethoxysilane to obtain highly hydrophobic wood surfaces with a water contact angle of 138° and good light stability. To simplify the reaction method, Zheng R [10] et al. directly hydrolysed crystalline TiCl_3 in saturated aqueous NaCl solution to grow rutile TiO_2 layered structures on the wood surface and then modified them using perfluorodecyltriethoxysilane, resulting in a water contact angle up to about 140° .

Noble metal modification can improve the catalytic activity of TiO_2 . Gao L [11] et al. loaded multifunctional Ag- TiO_2 composite films onto wood substrates via hydrothermal synthesis and silver mirror reaction and then modified them using perfluorodecyltrimethoxysilane; the water contact angle was increased to 153.2° , which greatly improved the water repellence of wood. Silver nitrate solution is expensive, whereas CaCO_3 is abundant, cheap and easy to control in terms of particle size and morphology. Gao [12] et al. added TiO_2 precursor solution to CaCO_3 solution to generate micro-nanocomposite particles, impregnated them into wood specimens and modified them with stearic acid. Due to the binding effect of roughness and stearic acid, air was trapped in the interstices and cavities of the wood surface, while water droplets were mainly in contact with the trapped air, resulting in superhydrophobic wood with a water contact angle of 155° . Based on this, Gao L [13] et al. constructed TiO_2 films on the wood surface by low-temperature hydrothermal methods and modified them with octadecyltrichlorosilane to achieve reversible control of the wettability of the wood surface.

Among the above-surface modification methods, the modification of wood surfaces with silica-titanium composite films can greatly improve the combustibility, thermal stability, dimensional stability, photocatalytic activity and hydrophobicity of wood surfaces, which is a more effective and environmentally friendly approach [14–17]. TiO_2 has excellent photocatalytic properties, but its catalytic capacity is limited when visible light is used as an energy input, and the catalytic effect of Bi_2O_3 can increase the photocatalytic

activity of TiO_2 [18,19]. However, in our previous study, we found that the modification of silica–titanium composite film on the surface of wood by Bi_2O_3 made the surface hydrophobicity of the composite film decrease, although it greatly increased its photocatalytic activity under visible light [19]. Therefore, in this paper, octadecyltrichlorosilane and polydimethylsiloxane were used to modify the surface hydrophobicity of wood loaded with Bi_2O_3 -doped silica–titanium composite films, and the surface roughness and surface free energy of the modified wood were tested to explore the reasons for the change in surface wettability of the wood and to analyse the effect of further hydrophobic modification on the photocatalytic activity of the bismuth-doped silica–titanium composite films.

2. Materials and Methods

2.1. Experimental Materials

The raw material was supplied from Liangfengjiang National Forest Park, Nanning, Guangxi. The logs were air-dried and further processed into small specimens measuring 40 mm (L) \times 40 mm (W) \times 5 mm (H). The smooth and defect-free specimens were then washed with distilled water, air-dried indoors (moisture content of about 15%) and stored for use. Tetrabutyl orthotitanate (TBOT, Analytical Reagent) and Vinyltriethoxysilane (VTES, Chemical Pure) were used as titanium and silicon sources, respectively, and Absolute alcohol (EtOH, Analytical Reagent) was used as a solvent; these were purchased from Wengjiang Chemical Reagent Co., (Yingde, China) and Damao Chemical Reagent Factory (Tianjin, China), respectively. Octadecyltrichlorosilane (OTS, 97%) and polydimethylsiloxane (PDMS, Analytical Reagent) were selected as hydrophobic modifiers and were purchased from Maclean Biochemical Technology Ltd. (Shanghai, China) and Damao Chemical Reagent Factory (Tianjin, China), respectively. Hexane (Analytical Reagent) was chosen as the solvent for OTS and PDMS and was purchased from Fuyu Fine Chemical Ltd. (Tianjin, China).

2.2. Hydrophobic Modification of Bi_2O_3 -Doped Si-Ti Composite Film on Wood Surface

VTES and TBOT were added to EtOH in the ratio of 1:3 under magnetic stirring, respectively, and after mixing the two solutions, a mixture of EtOH, H_2O and HNO_3 was added and stirred vigorously for 10 min to obtain liquid A. BiCl_3 was weighed at a titanium/bismuth molar ratio of 1:0.015, then dissolved in a mixture of 0.2 mol EtOH and 0.1 mol HNO_3 and stirred vigorously for 10 min to obtain liquid B. In the next step, solution B was slowly dripped into solution A, stirred vigorously for 1 h and then left to form a sol at room temperature. The sol was evenly painted on the surface of the wood and painted for the second time after 1 h. After ageing for 24 h, the wood specimen was dried at 100 °C for 6 h in a constant-temperature drying oven and then cooled to room temperature to obtain the surface-loaded Bi_2O_3 -doped silicon and titanium composite membrane [19]. OTS and PDMS solutions of 0.2%, 0.5%, 1%, 2% and 3% *v/v* were prepared under magnetic stirring using hexane as a solvent. The wood specimens were then dipped in different volume fractions of OTS-modified solution in a water bath at 50 °C for 2 h. The specimens were washed repeatedly with hexane, left at room temperature for 1 h to evaporate and then dried at 100 °C for 3 h. Finally, the specimens were removed and brought to room temperature for subsequent testing. Wood samples not treated with OTS and PDMS modification were used as controls (CK).

2.3. Characterisation of Structure and Properties

The surface morphology of hydrophobically modified wood samples was observed by stereomicroscope, and the static contact angle of distilled water on a wood surface was measured using a Cruise Contact Angle Meter (Hamburg, Germany). The volume of water droplets used for the test was 5 μL , and the contact angle was determined after the droplets remained on the wood surface for 10 s. The measuring temperature and relative humidity were 20 ± 1 °C and $65 \pm 3\%$, respectively, and five points were examined for each sample

and three samples for each treatment. Finally, the average value was taken as the contact angle of the wood surface.

The wettability of a solid surface was determined by its chemical composition and micromorphological structure [20]; the smaller the free energy of the solid surface, the less likely it is to be wettable by liquids and vice versa. Whereas solid surface roughness and microstructure are decisive conditions for the preparation of superhydrophobic surfaces, it is speculated that increasing surface roughness can improve surface hydrophobicity according to the contact angle theory model of Wenzel [21] and Cassie [22]. Therefore, the determination and calculation of surface roughness and surface free energy of hydrophobically modified wood specimens are necessary.

Based on the results of the surface wettability characterisation, FTIR characterisation was carried out on a set of wood samples with the best hydrophobic modification by OTS and PDMS, respectively. The tests were carried out using the KBr method. A certain amount of silica–titanium composite film and wood powder was scraped through a 100-mesh sieve, dried to absolute dryness, mixed with KBr at a volume ratio of 1:100, ground homogeneously and then formed into transparent circular flakes through a pressing machine. The chemical structure of SiO₂ and TiO₂ in the composite film and their bonding to the wood surface were analysed by a Fourier Transform Infrared (Rigaku Corporation, Tokyo, Japan) spectrometer. The main test conditions were as follows: scanning range 4000–400 cm^{−1} and scanning number 32.

The cross-grain roughness of the modified wood specimens was tested by a surface roughness tester using the stylus method [23], and each specimen was tested three times, with three specimens being tested per treatment, and finally, the average value was taken. The OWRK Equation (1) was used for the calculation of the surface free energy of the Bi₂O₃ doped silica–titanium composite film on the surface of the wood, as well as its polar and non-polar (dispersion) components. Since the formula contains two unknowns, it is necessary to obtain the surface tension and its components for two known liquids as well as the contact angle values for the corresponding liquids. Distilled water and diiodomethane were used in this study.

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p} \quad (1)$$

The best hydrophobic OTS- and PDMS-modified wood specimens were selected for visible light photocatalytic activity testing. The details and steps of the experiment are as follows [19].

Degradation of rhodamine B: A 500 W xenon lamp ($\lambda > 420$ nm) was used as the light source for this experiment, and the modified wood was immersed in 30 mL of a 10 mg/L solution of rhodamine B. The sample was kept in the dark for 30 min, and the concentration of rhodamine B was calculated to be the initial concentration C_0 . The lamp was then switched on and the composite membrane was adjusted to face the centre of the light source vertically at a distance of 40 cm. The reaction temperature was controlled at 20–30 °C, and the light time was 180 min. Subsequently, the absorbance of the remaining solution at a wavelength of 554 nm was measured, and the concentration of the solution was obtained using the standard curve of Figure 1. Finally, the degradation rate of rhodamine B by modified wood was calculated according to Equation (2).

$$D = [(C_0 - C)/C_0] \times 100\% \quad (2)$$

Degradation of the gas formaldehyde: 3 mL of a standard solution of formaldehyde at a concentration of 0.02 mg/mL was passed through a formaldehyde generator and converted to gas into the test apparatus. After the modified wood was placed into the reaction chamber and adsorbed in the dark for 30 min, the formaldehyde gas concentration was measured with a formaldehyde detector as the initial concentration C_0 . The subsequent steps and calculation formulae were the same as those for the rhodamine B experiment.

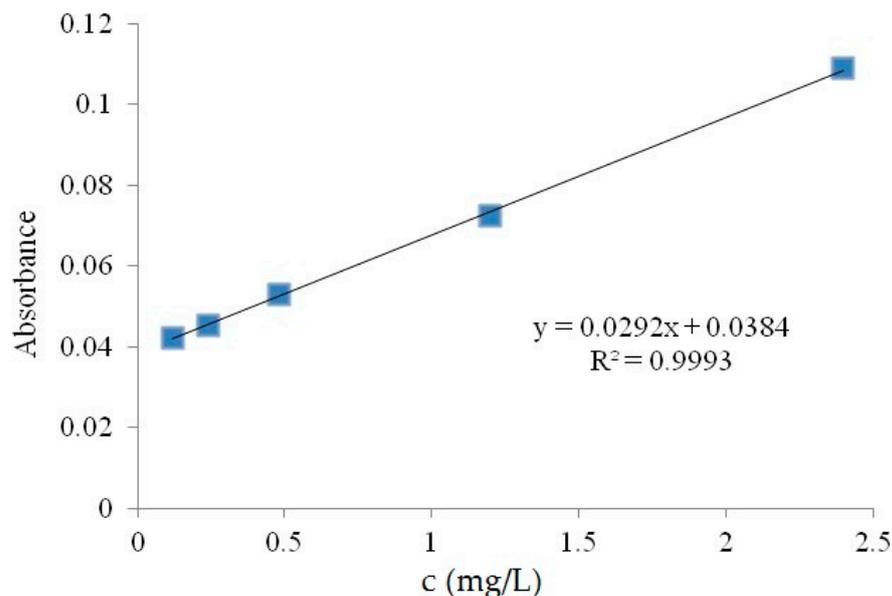


Figure 1. The standard curve of rhodamine B aqueous solution.

3. Results and Discussion

3.1. Surface Morphology Analysis

Figure 2 shows the somatoscopic microscopic images of wood specimens modified with different volume fractions of OTS and PDMS. The volume fractions of OTS (a, c, e, g, i) and PDMS (b, d, f, h, j) are increasing in order. As can be seen from Figure 2, there is no significant difference in the macroscopic surface of wood specimens treated with different hydrophobic modifiers. However, compared with the non-hydrophobically modified treatment, the small cracks on the surface were reduced, indicating that OTS and PDMS were successfully loaded on the surface of the composite film by chemical combination or physical adsorption in the hydrophobically modified treatment, filling the defects and possibly increasing the microscopic roughness on the surface of the wood specimens, thus improving the hydrophobicity of the wood specimens.

3.2. Surface Wettability Analysis

As can be seen from Figure 3, the contact angle of the bismuth-doped silica–titanium composite film on the wood surface modified with different volume fractions of both OTS and PDMS was significantly improved. In addition, the contact angle of the OTS hydrophobically modified wood specimens increased with the increase in the volume fraction of OTS. The contact angle of the samples reached the maximum value when the volume fraction of OTS was 2%, while the contact angle basically ceased to increase when the volume fraction was 3%, indicating that 2% of OTS modifier can make the surface of the wood specimens achieve a high degree of hydrophobicity. Similarly, the contact angle of the PDMS hydrophobically modified wood specimens increased with the increase in the volume fraction of PDMS and reached the maximum when the volume fraction was 3%, but its maximum value was lower than that of the OTS modification, which indicated that the effect of OTS hydrophobic modification was better than that of PDMS. In addition, the hydrophobicity of wood modified with either OTS or PDMS was superior to that of wood modified with methyl methacrylate (MMA, 99.5%) [24], although the hydrophobic modification of the wood in this experiment required a shorter period of time.

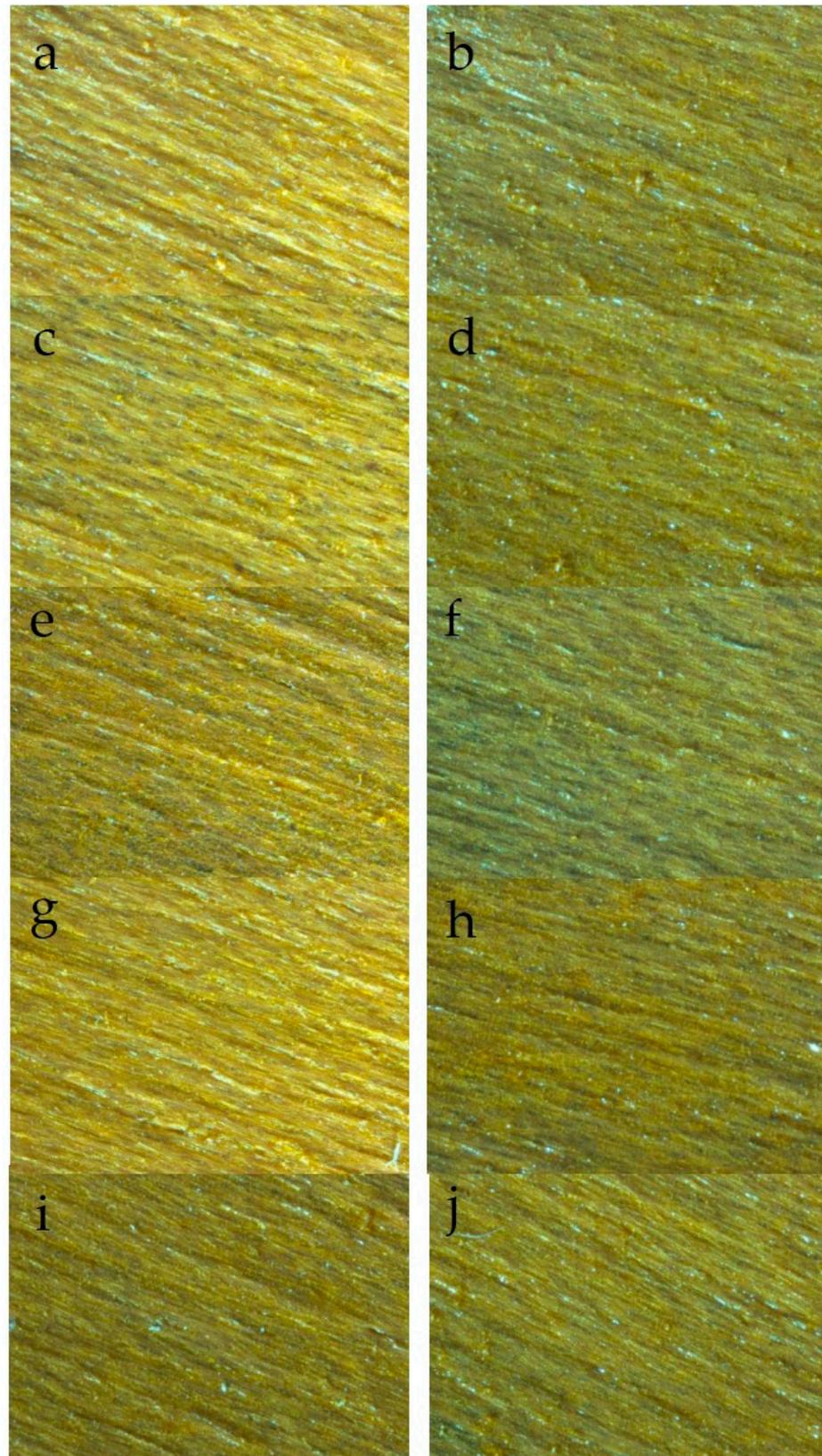


Figure 2. Holographic microscopy of modified wood specimens with different volume fractions of OTS (a,c,e,g,i) and PDMS (b,d,f,h,j).

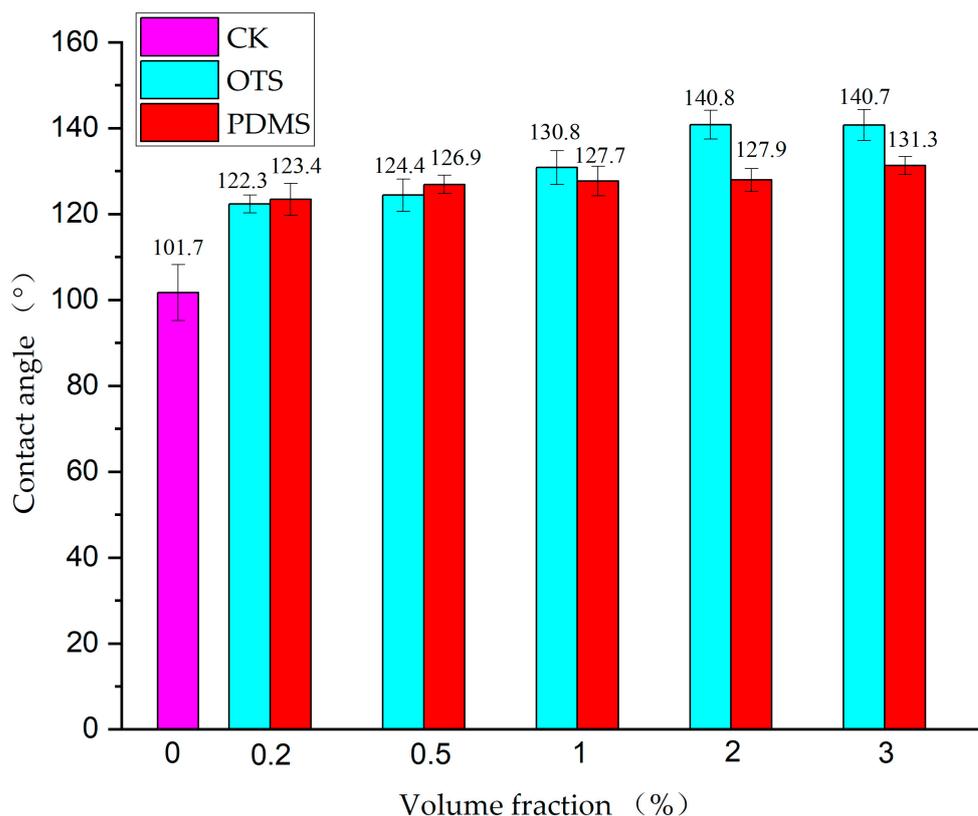


Figure 3. Contact angles of unmodified and different volume fractions of OTS- and PDMS-modified wood samples.

In this experiment, the silica–titanium composite film was prepared using the sol-gel method with mild reaction conditions, and the surface hydrophobic modification did not require high-temperature and high-pressure treatments; in addition, the preparation process was free of toxic gases and wastewater. In particular, the OTS modification treatment made the contact angle of the wood surface reach the maximum value of 140° in a short treatment time, indicating that the method has a certain low energy consumption and environmental protection.

3.3. FTIR Analysis

Figure 4 shows the infrared spectra of the surface-loaded Bi_2O_3 -doped silica–titanium composite film before and after hydrophobic modification of the wood specimen by 2% OTS n-hexane solution and 2% PDMS n-hexane solution, respectively. As can be seen from the figure, the peak near 3424 cm^{-1} is the stretching vibration peak of $-\text{OH}$, and the peak intensity is weakened and the peak shape is narrowed after 2% OTS and 2% PDMS treatments; thus, it is presumed that the amount of $-\text{OH}$ on the surface of the wood specimen is reduced. The peaks near 2919 cm^{-1} and 2850 cm^{-1} are the stretching vibration peaks of C-H in $-\text{CH}_2-$ [25], and the intensity of the peaks is strengthened after the treatments, and the vibration peak intensity of the wood specimen treated with 2% OTS is stronger than that of the wood specimen treated with 2% PDMS. The intensity of the vibrational peaks was stronger than that of the 2% PDMS-treated wood specimen, and it is presumed that the long-chain alkyl groups of OTS were successfully grafted on the surface of the composite film, which is the main reason for the hydrophobicity [13]. The peak near 1625 cm^{-1} may be attributed to the telescopic vibrational peak of $\text{C}=\text{C}$, and the peaks near 1550 cm^{-1} and 1300 cm^{-1} may be ascribed to the stretching vibration peak of $\text{Bi}-\text{O}$ [26]. In addition, the sharp peak at 1384 cm^{-1} is the stretching vibration peak of $-\text{NO}_3$, and the intensity of the vibration is weakened after hydrophobic treatment, which may be caused by secondary drying. The peaks near 1118 cm^{-1} and 1029 cm^{-1} may be the asymmetric

telescopic vibration peaks of Si-O-Si [27]. The peak near 900 cm^{-1} may be the telescopic vibration peak of Ti-O-Si [28], and the peak near 550 cm^{-1} may be the vibration peak of the Ti-O-Ti absorption peak.

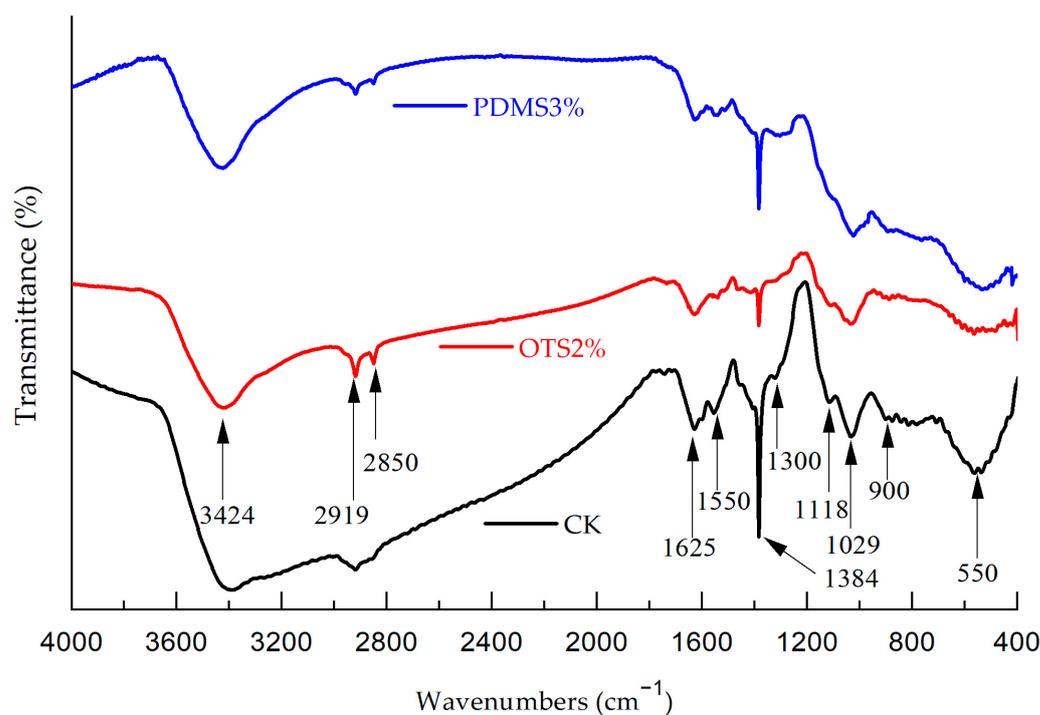


Figure 4. The FTIR spectra of wood samples before (CK) and after hydrophobic modification (PDMS3%, OTS2%).

3.4. Surface Roughness Analysis

Surface roughness refers to the degree of surface roughness in the range of microscopic fluctuations [29], and wood surface roughness is one of the important factors affecting its surface wettability. Parameters for assessing surface roughness such as the arithmetic mean deviation of the contour (R_a), the 10-point height value of the contour (R_z), the maximum height of the contour (R_y), and the average spacing of the microscopic unevenness of the contour (S_m) can be obtained from surface roughness testers [29,30]. Among them, R_a is the most commonly used, so it was used in this study to characterise the change in surface roughness of Bi_2O_3 -doped silica–titanium composite films on hydrophobically modified wood surfaces. It was not difficult to find that OTS and PDMS had a significant effect ($t < 0.05$) on the change in roughness of wood before and after modification by t -test, whereas there was no significant difference ($t > 0.05$) in the change in roughness of wood after hydrophobic modification with OTS and PDMS, respectively.

It can be seen from Figure 5 that the surface roughness of the hydrophobically modified wood specimens increased with the increase in the volume fraction of OTS and PDMS, both of which were larger than that of the non-hydrophobically modified wood specimens by $3.71\text{ }\mu\text{m}$. The surface roughness of the OTS-modified wood specimens with volume fractions of 2% and 3% were similar, and the surface roughness of the PDMS-modified wood specimens with volume fractions of 1% and 2% were similar, both of which differed by only $0.02\text{ }\mu\text{m}$. It can also be seen that when the volume fractions of the hydrophobic modifier were 0.2% and 0.5%, the roughness values of OTS- and PDMS-modified wood specimens were close to each other, but the roughness of PDMS was slightly larger; when the volume fractions continued to increase, the roughnesses of the OTS-modified wood specimens were all larger than those of the PDMS-modified wood specimens. This is consistent with the results of the contact angle test, indicating that after hydrophobic modification, OTS and PDMS grafted on the surface of the composite film, increasing the roughness of the

surface of the composite film, and thus improving the hydrophobicity of the composite film, which is consistent with the Wenzel model.

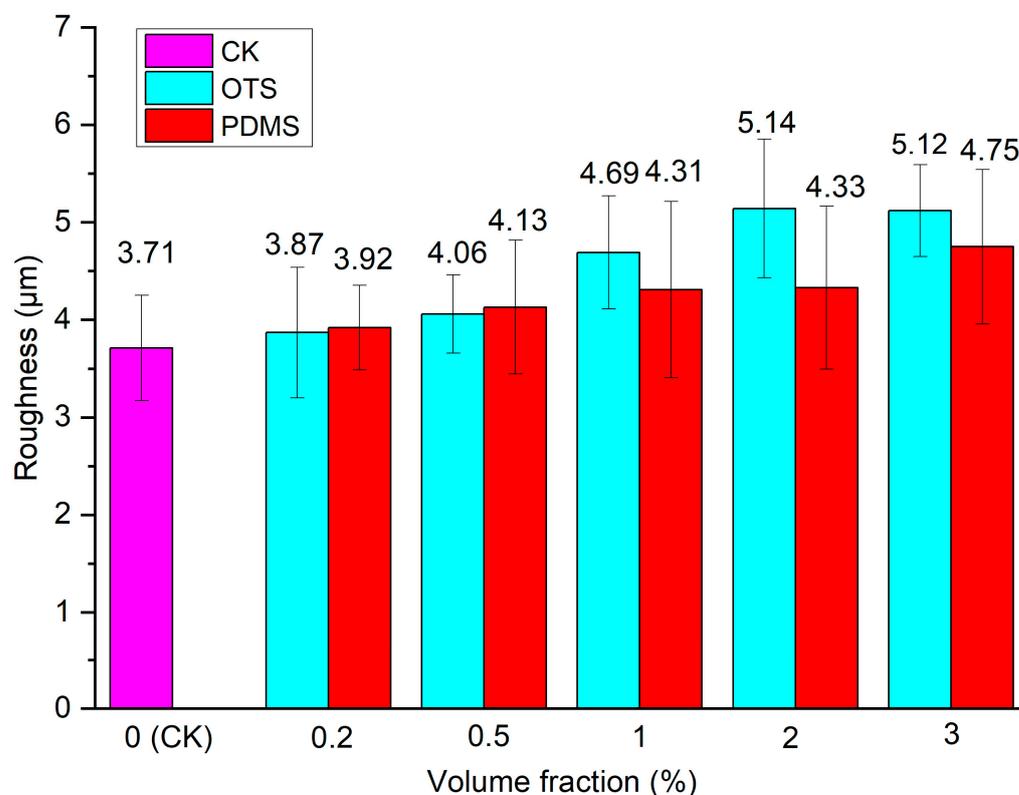


Figure 5. The change in roughness on the wood surface before and after hydrophobic modification.

3.5. Surface Free Energy Analysis

Except for surface roughness, surface free energy is also an important factor affecting the wettability of wood surfaces. The wood surface free energy can be obtained according to the contact angle value of liquid on the wood surface combined with different calculation equations. In this study, the geometric average method was used to calculate the surface free energy, and the test liquid was distilled water and diiodide.

The surface free energy and the component values of γ_L^d and γ_L^p are shown in Table 1. The contact angle of distilled water and diiodomethane on hydrophobically modified and unmodified wood surfaces loaded with silica–titanium composite films is shown in Table 2. The surface free energies and their γ_L^d and γ_L^p components of unmodified and modified wood samples with different volume fractions OTS and PDMS were calculated according to the geometric averaging method, and the results are shown in Table 3. It is obvious that the surface free energy of the bismuth-doped silica–titanium composite film on the wood surface modified with both OTS and PDMS is reduced, indicating that both fluids improve the hydrophobicity of the composite film. According to Table 2, compared with the contact angles of water on the surface of different wood samples, the contact angles of diiodomethane are always smaller than those of water because the surface tension of diiodomethane (50.8 mJ/m^2) is smaller than that of water (72.8 mJ/m^2). It can be seen from Table 3 that the surface free energy of wood samples decreases gradually with the increase in volume fraction, regardless of whether OTS or PDMS is used. For OTS-modified wood samples, with the increase in OTS volume fraction, the proportion of chromatic dispersion component γ_s^p/γ_s on the surface of wood samples gradually increases, and the proportion of polarity component γ_s^d/γ_s gradually decreases, while the volume fraction does not change from 2% to 3%, and the surface free energy of the two is equal. For PDMS-modified wood samples, with the increase in volume fraction, the proportion of

dispersion component γ_s^d/γ_s on the surface of wood samples shows an increasing trend, while the proportion of polarity component γ_s^p/γ_s shows a decreasing trend. There was no change in γ_s^d/γ_s and γ_s^p/γ_s at volume fractions of 0.5%, 1% and 2%, probably because the changes were small and the results were equal after rounding. In general, the surface free energy of modified wood samples decreased because of the decrease in polar force.

Table 1. Surface tension and its components in the liquids.

Liquid	Surface Tension (mJ/m ²)						
	γ_L	γ_L^d	γ_L^p	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
Distilled water	72.8	21.8	51.0	21.8	51.0	25.5	25.5
Diiodomethane	50.8	50.8	0	50.8	0	0	0

Table 2. Contact angle of distilled water and diiodomethane on hydrophobically modified and unmodified wood surfaces loaded with silica–titanium composite films.

Test Solution	Modifiers	Contact Angle/°					
		0% (CK)	0.2%	0.5%	1%	2%	3%
Distilled water	OTS	101.7	122.3	124.4	130.8	140.8	140.7
	PDMS		123.4	126.9	127.7	127.9	131.3
Diiodomethane	OTS	94.5	113	114.9	121.1	128.5	128.5
	PDMS		115.7	118.6	119.5	120.2	121.3

Table 3. Surface free energy and γ_s^p , γ_s^d component of unmodified and modified wood samples with different volume fractions of OTS and PDMS.

Surface Free Energy mJ/m ²	OTS						PDMS					
	CK	0.2%	0.5%	1%	2%	3%	0.2%	0.5%	1%	2%	3%	
γ_s	5.21	3.13	2.94	2.37	1.62	1.62	3.00	2.69	2.61	2.58	2.33	
γ_s^d	3.29	2.17	2.07	1.73	1.35	1.35	2.02	1.86	1.81	1.77	1.72	
γ_s^p	1.92	0.96	0.87	0.64	0.27	0.28	0.97	0.82	0.80	0.81	0.62	
γ_s^d/γ_s	0.63	0.69	0.70	0.73	0.83	0.83	0.67	0.69	0.69	0.69	0.74	
γ_s^p/γ_s	0.37	0.31	0.30	0.27	0.17	0.17	0.33	0.31	0.31	0.31	0.26	

3.6. Photocatalytic Activity Evaluation

Figures 6 and 7 show the decolourization rate of rhodamine B and the degradation rate of gaseous formaldehyde of Bi₂O₃-doped Si-Ti composite film under visible light before and after modification. As can be seen from the figure, after OTS and PDMS hydrophobic modification, the decolourization rate of rhodamine B and formaldehyde degradation rate of Bi₂O₃-doped Si-Ti composite film on the wood surface slightly decreased, which may be because the load of OTS and PDMS on the composite film surface affected the light absorption performance of TiO₂. However, the photocatalytic activity of the Bi₂O₃-doped Si-Ti composite film on the wood surface is still high, and the degradation rate of rhodamine B and formaldehyde is still above 90%, indicating that hydrophobic modification has very little effect on the photocatalytic activity of Bi₂O₃-doped Si-Ti composite films on wood surfaces.

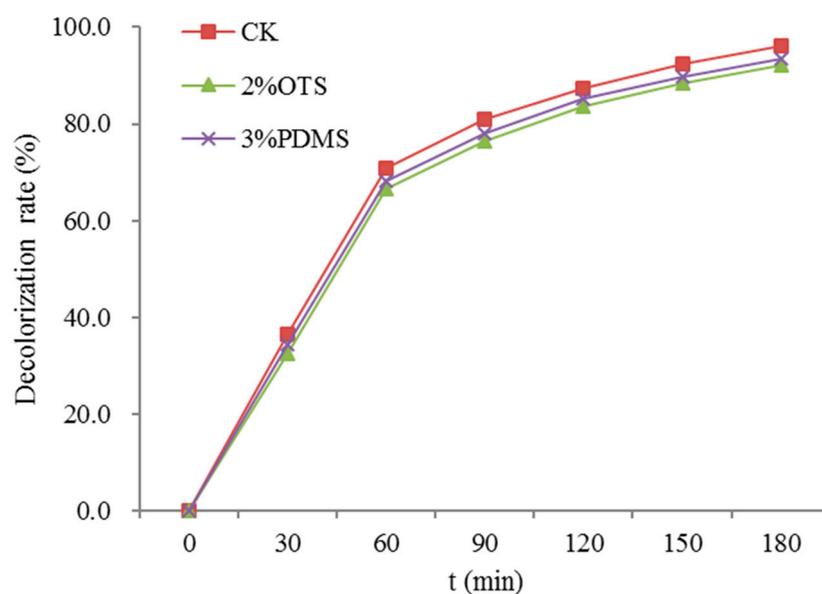


Figure 6. Decolourization of rhodamine B by Bi_2O_3 -doped Si-Ti composite film before and after modification.

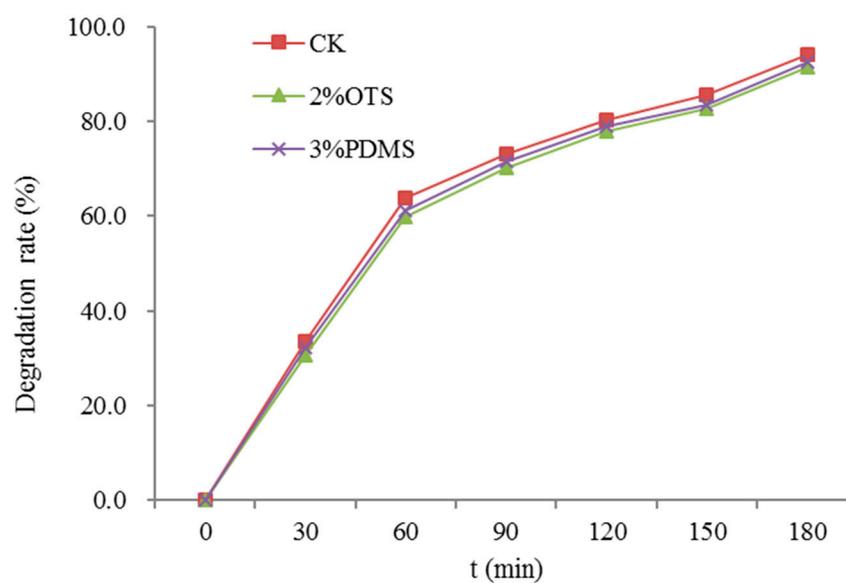


Figure 7. Degradation of formaldehyde by Bi_2O_3 -doped Si-Ti composite film before and after modification.

4. Conclusions

Wood specimens loaded with Bi_2O_3 -doped silica–titanium composite films ($n(\text{Ti}):n(\text{Bi}) = 1:0.015$) were prepared and hydrophobically modified with octadecyltrichlorosilane (OTS) and polydimethylsiloxane (PDMS) *n*-hexane solutions. The results showed that the water contact angle and surface roughness of the hydrophobically modified wood samples increased with the increase in volume fraction, but the overall effect of hydrophobic modification by OTS was better than that of PDMS, and the maximum water contact angle of the OTS samples could reach 140.8° when the volume fraction of OTS was 2%. FTIR analysis showed that there was no obvious change in the chemical groups before and after the hydrophobic treatment, but the intensity of the telescopic vibration peak of $-\text{OH}$ was weakened, and the intensity of the telescopic vibration peak of $-\text{CH}_2-$ was strengthened, which was the reason for the enhancement of hydrophobicity. In addition,

the surface free energies of the modified wood specimens were all reduced, which was mainly due to the reduction in the polar force. Overall, OTS and PDMS can improve the surface hydrophobicity of wood specimens by increasing their surface roughness and decreasing their surface free energy. Finally, the hydrophobically modified Bi₂O₃-doped silica–titanium composite film still possessed high photocatalytic activity and degraded rhodamine B and gaseous formaldehyde by more than 90%.

Author Contributions: Z.L. and P.W. conceived and designed the experiments; S.C. and L.G. drafted the manuscript; Y.F. and S.C. participated in data analysis; S.C. carried out the laboratory work. All authors have read and agreed to the published version of the manuscript.

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References

1. Hsieh, C.; Chang, B.; Lin, J. Improvement of water and oil repellency on wood substrates by using fluorinated silica nanocoating. *Appl. Surf. Sci.* **2011**, *257*, 7997–8002. [[CrossRef](#)]
2. Wang, J.; Lu, Y.; Chu, Q.; Ma, C.; Cai, L.; Shen, Z.; Chen, H. Facile construction of superhydrophobic surfaces by coating fluoroalkylsilane/silica composite on a modified hierarchical structure of wood. *Polymers* **2020**, *12*, 813. [[CrossRef](#)]
3. Tan, Y.; Wang, K.; Dong, Y.; Zhang, W.; Zhang, S.; Li, J. Bulk superhydrophobicity of wood via in-situ deposition of ZnO rods in wood structure. *Surf. Coat. Technol.* **2020**, *383*, 125240. [[CrossRef](#)]
4. Wang, K. Preparation and Mechanism of Superhydrophobic Wood Based on Surface Micro/Nano Structure Design. Master's Thesis, Beijing Forestry University, Beijing, China, 2019; pp. 65–76.
5. Yang, T.; Xia, M.; Chen, S.; Mu, M.; Yuan, G. Enhancing the thermal stability of silica-mineralized wood via layer-by-layer self-assembly. *J. Therm. Anal. Calorim.* **2021**, *145*, 309–318. [[CrossRef](#)]
6. Liu, M.; Qing, Y.; Wu, Y.; Liang, J.; Luo, S. Facile fabrication of superhydrophobic surfaces on wood substrates via a one-step hydrothermal process. *Appl. Surf. Sci.* **2015**, *330*, 332–338. [[CrossRef](#)]
7. Yang, R.; Zuo, S.; Song, B.; Mao, H.; Huang, Z.; Wu, Y.; Cai, L.; Ge, S.; Lian, H.; Xia, C. Hollow mesoporous microspheres coating for super-hydrophobicity wood with high thermostability and abrasion performance. *Polymers* **2020**, *12*, 2856. [[CrossRef](#)]
8. Wang, C.; Zhang, M.; Xu, Y.; Wang, S.; Liu, F.; Ma, M.; Zang, D.; Gao, Z. One-step synthesis of unique silica particles for the fabrication of bionic and stably superhydrophobic coatings on wood surface. *Adv. Powder Technol.* **2014**, *25*, 530–535. [[CrossRef](#)]
9. Wang, X.; Liu, S.; Chang, H.; Liu, J. Sol-gel deposition of TiO₂ nanocoatings on wood surfaces with enhanced hydrophobicity and photostability. *Wood Fiber Sci.* **2014**, *46*, 109–117.
10. Zheng, R.; Tshabalala, M.; Li, Q.; Wang, H. Construction of hydrophobic wood surfaces by room temperature deposition of rutile (TiO₂) nanostructures. *Appl. Surf. Sci.* **2015**, *328*, 453–458. [[CrossRef](#)]
11. Gao, L.; Gan, W.; Xiao, S.; Zhan, X.; Li, J. A robust superhydrophobic antibacterial Ag-TiO₂ composite film. *Ceram. Int.* **2016**, *42*, 2170–2179. [[CrossRef](#)]
12. Gao, Z.; Ma, M.; Zhai, X.; Zhang, M.; Zang, D.; Wang, C. Improvement of chemical stability and durability of superhydrophobic wood surface via filming TiO₂ coated CaCO₃ micro-nano-composite particles. *RSC Adv.* **2015**, *5*, 63978–63984. [[CrossRef](#)]
13. Gao, L.; Lu, Y.; Cao, J.; Li, J.; Sun, Q. Reversible Photocontrol of Wood-Surface Wettability Between Superhydrophilicity and Superhydrophobicity Based on a TiO₂ Film. *J. Wood Chem. Technol.* **2015**, *35*, 365–373. [[CrossRef](#)]
14. Ma, X.; Zhou, W.; Chen, Y. Structure and photocatalytic properties of Mn-doped TiO₂ loaded on wood-based activated carbon fiber composites. *Materials* **2017**, *10*, 631. [[CrossRef](#)] [[PubMed](#)]
15. Hung, K.; Wu, J. Characteristics and thermal decomposition kinetics of wood-SiO₂ composites derived by the sol-gel process. *Holzforschung* **2017**, *71*, 233–240. [[CrossRef](#)]
16. Xu, E.; Zhang, Y.; Lin, L. Improvement of mechanical, hydrophobicity and thermal properties of Chinese fir wood by impregnation of nano silica sol. *Polymers* **2020**, *12*, 1632. [[CrossRef](#)]
17. Yu, L.; Cai, J.; Wang, Y.; Tang, Z.; Zhu, J. Improved dimensional stability of nano-SiO₂/wax modified ACQ-treated southern pine. *Bioresources* **2017**, *12*, 7515–7524. [[CrossRef](#)]
18. Dirna, F.; Rahayu, I.; Zaini, L.; Darmawan, W.; Prihatini, E. Improvement of fast-growing wood species characteristics by MEG and nano SiO₂ impregnation. *J. Korean Wood Sci. Technol.* **2020**, *48*, 41–49. [[CrossRef](#)]
19. Liu, Z.; Xu, J.; Cheng, S.; Qin, Z.; Fu, Y. Photocatalytic performance and kinetic studies of a wood surface loaded with Bi₂O₃-doped silicon–titanium composite film. *Polymers* **2023**, *15*, 25. [[CrossRef](#)]

20. Li, X.; Liu, Y. Control and preparation to wettability of material surfaces. *Mat. Eng.* **2008**, *4*, 74–80.
21. Wenzel, R. Resistance of solid surfaces to wetting by water. *Ind. Eng. Chem.* **1936**, *28*, 988–994. [[CrossRef](#)]
22. Cassie, A.-B.-D.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551. [[CrossRef](#)]
23. Liu, B.; Feng, Q.; Kuang, C. Survey of measurement methods for surface roughness. *Opt. Instrum.* **2004**, *26*, 54–58.
24. Fu, Y.; Li, G.; Yu, H.; Liu, Y. Hydrophobic modification of wood via surface-initiated ARGET ATRP of MMA. *Appl. Surf. Sci.* **2012**, *258*, 2529–2533. [[CrossRef](#)]
25. Sun, X.; Li, L.; Xu, X.; Song, G.; Tu, J.; Yan, P.; Zhang, W.; Hu, K. Preparation of hydrophobic SiO₂/PTFE sol and antireflective coatings for solar glass cover. *Optik* **2020**, *212*, 164704. [[CrossRef](#)]
26. He, F.; Wang, J.; Deng, D. Effect of Bi₂O₃ on structure and wetting studies of Bi₂O₃-ZnO-B₂O₃ glasses. *J. Alloy Compd.* **2011**, *509*, 6332–6336. [[CrossRef](#)]
27. Queeney, K.T.; Weldon, M.K.; Chang, J.P.; Chabal, Y.J.; Gurevich, A.B.; Sapjeta, J.; Opila, R.L. Infrared spectroscopic analysis of the Si/SiO₂ interface structure of thermally oxidized silicon. *J. Appl. Phys.* **2000**, *87*, 1322–1330. [[CrossRef](#)]
28. Zhou, L.; Yan, S.; Tian, B.; Zhang, J.; Anpo, M. Preparation of TiO₂-SiO₂ film with high photocatalytic activity on PET substrate. *Mater. Lett.* **2006**, *60*, 396–399. [[CrossRef](#)]
29. Qin, Q.; Liu, S. Surface Roughness. *Plat. Finish.* **2009**, *31*, 32–34.
30. Wang, M.; Wang, J.; Li, L. Analysis of wood surface roughness. *J. Beijing For. Univ.* **2005**, *27*, 14–18.

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